WATER BINDING IN HIDE MATERIALS*

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ABSTRACT

Differential Thermal Analysis (DTA) was used to study water binding in hides and leathers. Water is bound to the collagen system (hides, tanning agents, and other additives used) with greater tenacity than the intermolecular bonds in water itself, since the peak due to water lost from the leather is observed above 100°C. The water is lost over a wide temperature range, indicating that a spectrum of binding energies is involved. Both the peak temperature and intensity are strongly dependent on the previous conditioning of the sample. This conditioning has a greater effect than the various tanning treatments. A "peak temperature heat of dehydration" was calculated from pressure-temperature diagrams. The values obtained for hide materials lie between the $\triangle H$ for liquid water and water bound in a crystalline hydrate.

INTRODUCTION

Most materials incorporate water within their structure. In the case of hide materials, this water has been described as free, associated, or bound within the leather-tannage complex (1), but little is actually known about water binding in collagen or other proteins. It has been recently reported for geological materials (2) that deterioration or breakdown once believed due to free water alternately freezing and thawing is actually due to effects caused by temperature changes in bound water. A study of cell tissue by nuclear magnetic resonance (3) revealed no changes below 0°C., where free water would be expected to freeze. In view of these recent developments and the role water and heat play in foot comfort, heat setting or "permanent set" of shoes and "hot dry shrinkage" of leather, a thermal study of water binding in leather was needed. One way is to study the loss of water or the dehydration of leather as it is heated. The loss of water on heating can be readily observed by differential thermal analysis, commonly abbreviated DTA. DTA records physical or chemical changes occurring in a sample compared with an inert reference material when both are

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heated at the same rate. Differential thermal analysis is also used to measure the shrinkage temperature of leather (4, 5). This, however, is an entirely different technique from the DTA method employed for bound water. Conventional shrinkage temperatures are always measured in an aqueous medium. For measurement of shrinkage temperature by DTA we add a 50 percent excess of water. But in this water binding study we wish to consider only the water within the leather structure. The samples are run *as is* in dry glass tubes — no water is added.

EXPERIMENTAL

Instrumentation.—The instrument used in this investigation was the duPont 900 Differential Thermal Analyzer.** The cell assembly consists of an aluminum or silver block with sample and reference holes placed symmetrically around a heater hole and a hole to accommodate the temperature-programming thermocouple which can be set for various heating rates. A plot of temperature differential ($\triangle T$) versus sample temperature (T) is obtained on an x-y recorder. The instrument is equipped to run samples under vacuum in its standard cell. Measurements under pressures higher than atmospheric were made in a specially constructed pressure cell. The details of this pressure cell have been reported (6).

The usual rate of heating was 10°C./min. Heating at 5°/min. produced the same peak temperatures as the 10°/min. rate. Peak temperatures were one degree higher with a 20°/min. rate.

The DTA sample and reference holders are glass tubes 25 mm in length and 4 mm in diameter. A typical leather sample was 8 mm long and weighed approximately 30 mg. Thin leather samples were folded in half with the flesh sides touching before placement in the sample tube. The sample thermocouple was placed in the center of the fold. A slit was made in the grain layer of thicker samples and the thermocouple placed in the slit. Very thick samples, such as sole leather, were sectioned and the piece containing the grain layer was slit for the thermocouple. Both sampling techniques gave identical peak temperatures. Slitting the flesh or the grain layer for placement of the thermocouple made no difference in peak temperature either.

Sample Conditioning.—All the leather samples were stored in a constant temperature-humidity room maintained at 23°C. and 50 percent R.H. This conditioning gave moisture levels of 11 to 16 percent for tanned, finished leathers. For further conditioning, samples were stored in desiccators over a sulfuric acid-water mixture which gives a constant three percent relative humidity, or over distilled water which would approximate 100 percent R.H. These latter conditions produced samples containing four to six percent moisture and 27–31 percent moisture for tanned, finished leathers.

**Mention of commercial firms and products does not constitute an endorsement over others of a similar nature not mentioned.

Time of conditioning was at least three days at any particular humidity. Samples left too long in the distilled water desiccator accumulated mold. The samples were cut and placed in the sample tubes before storage in desiccators to minimize handling after conditioning. All tests on one sample conditioned in a particular manner were run in one day, for greater accuracy. Peak temperatures of the driest samples shifted over the course of a day because of changes in moisture levels from opening desiccators and exposing samples to room conditions while preparing the cell for a run, even when cells were first flushed with nitrogen.

RESULTS

Typical DTA Thermograms of Bound Water in Leather Systems.—Figure 1 illustrates thermograms obtained by DTA on samples of a chrome-tanned leather containing 15 percent moisture. Curve 1 shows a sample of this leather heated without the addition of water. A strong, broad peak with a maximum at 117°C. (243°F.) results. This is the peak due to loss of water bound

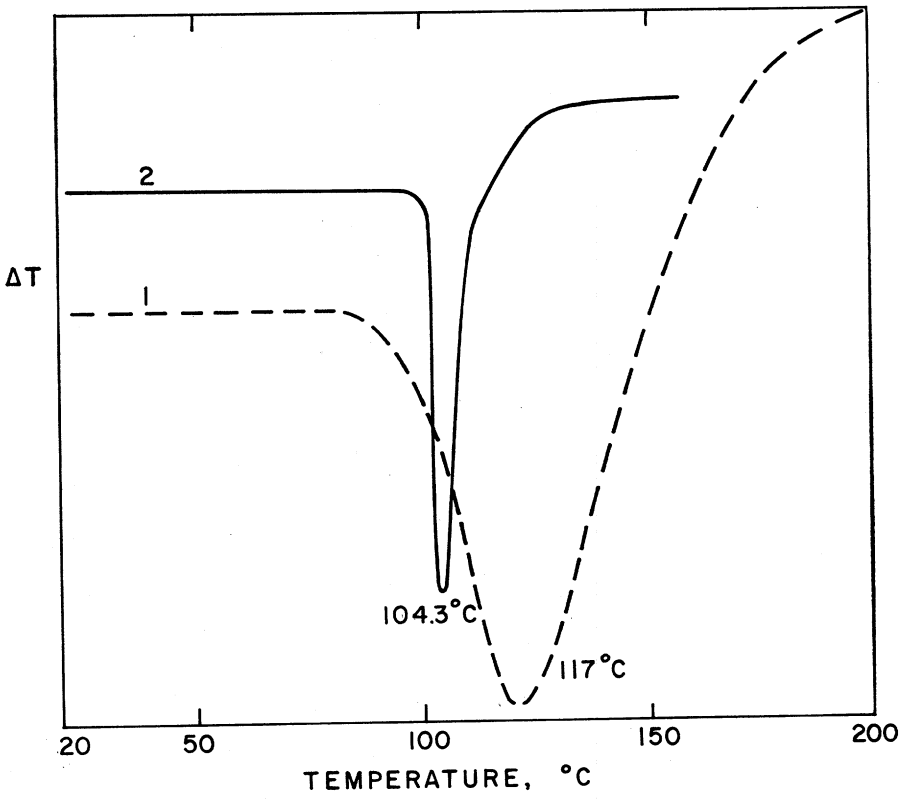

FIGURE 1.—Curve 1. Bound water DTA thermogram of chrome-tanned leather. Curve 2. Conventional DTA shrinkage thermogram of chrome-tanned leather.

within the leather. Curve 2 is the conventional shrinkage thermogram obtained on another sample of the same leather run immersed in water. It exhibits the narrow temperature range and sharp peak which is characteristic of melting. The conventional shrinkage temperature of this particular sample taken from the peak of the thermogram is 104.3°C. (220°F.).

Figure 2 shows the same chrome-tanned leather compared with liquid water. Curve 1 is the bound water thermogram of the leather. Curve 2 is the thermogram obtained by boiling a quarter of a milligram of distilled water. The bound water peak is very broad compared with the boiling water peak.

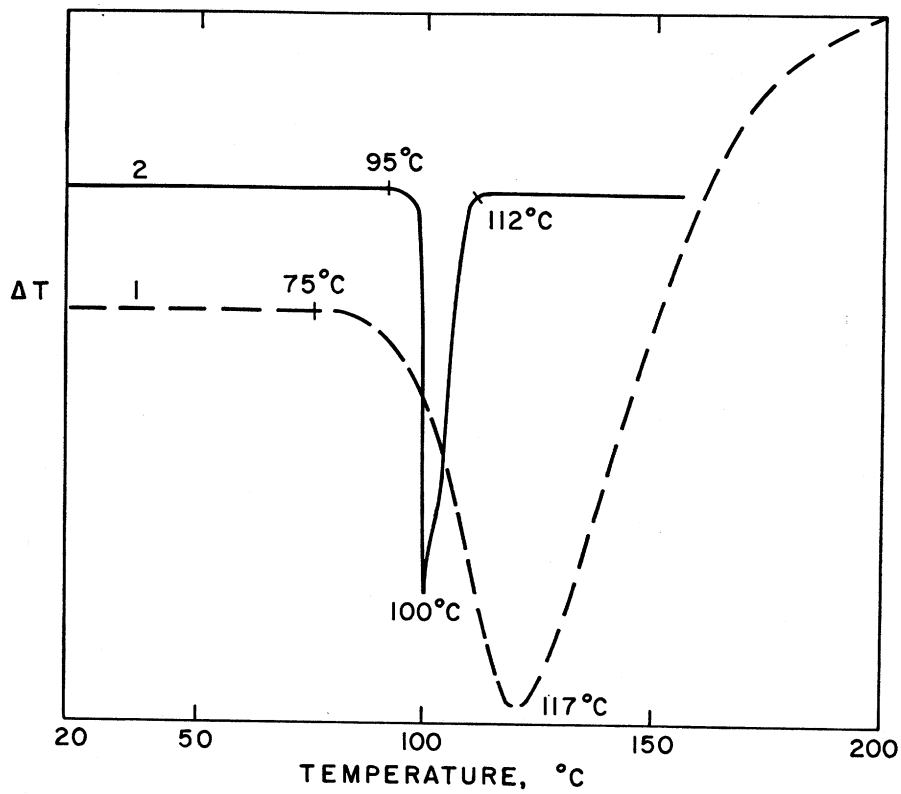

FIGURE 2.—Curve 1. Bound water DTA thermogram of chrome-tanned leather. Curve 2. DTA thermogram of liquid water.

The boiling temperature of water obtained by DTA is 100°C., the expected value at atmospheric pressure. The bound water peak shown in Curve 1 is at 117°C. at atmospheric pressure. The fact that the peak temperature of the bound water in the leather sample is above 100°C. indicates that some of the water is bound to the collagen system with more energy than the water-water bond in

liquid water. The term collagen system will be used throughout this paper to refer to leather, collagen or calfskin containing water, tanning agents, oil, finishes and other such additives. Not all of the water is bound with the same degree of tenacity, however. This can be seen from the broad temperature range over which the water is lost from the sample, by comparison of the onset temperature and the return to baseline in both curves. The onset temperature is the sample temperature at which the slope of the thermogram first departs from the baseline. This corresponds to the first indication that a change in the sample is starting to take place. In the boiling water thermogram the onset temperature is 95°C., only 5° below the peak temperature, while the onset temperature in the leather thermogram is 75°C., 43° below the peak temperature of 117°. The water is lost from the leather over a very broad temperature range, indicating that some water molecules are more loosely bound to the leather than others.

The boiling water thermogram returns to its baseline at 112°C. The entire peak covers a temperature range of 17°C., from 95 to 112°C. The bound water thermogram, however, does not level off in the temperature range studied. It levels off above 200°C. This gradual change over the broad temperature range of 75 to +200°C. is due to the disappearance of the water phase in the leather and indicates that the change is gradual and undoubtedly involves a spectrum of binding energies.

None of the bound water thermograms show any sharp change at 100°C. Liquid water is not present even in small amounts or the sensitivity of the instrument would detect it. Less than one hundredth of a milligram of liquid water would be detectable as a bump or irregularity in the curve. The bound water thermograms were also compared with those of salt solutions. The boiling point observed by DTA for a 1 molal solution of sodium chloride was slightly above 100°C., and like water itself, the salt solution thermograms exhibit sharp peaks over a narrow temperature range from onset to return to baseline. The broad peak at 117°C. in leather samples cannot be explained as a boiling point elevation of water by dissolved salts.

This 117°C. peak is due to loss of water on heating, because vacuum drying of the leather sample at 60°C. for 18 hours has always resulted in a completely horizontal line in the thermogram in the temperature range below 200°C. There is no peak if there is no water present in the leather. Returning the vacuum-dried sample to a 50 percent R.H. room restores the sample to its former condition, that is, the peak reappears at 117°C. Secondly, the peak temperature varies with the humidity at which the samples were conditioned; and third, the peak temperature also changes if the sample is run under pressure or vacuum.

Effect of Conditioning.—The results of the conditioning treatments are shown in Figure 3. All these runs were made at atmospheric pressure on different samples of the same chrome-tanned leather. In addition to the shift in peak temperature with humidity, the effect on the relative peak heights can be readily

observed. The sample with the lowest moisture content (6 percent water) has the smallest peak but at the highest temperature, 138°C., as seen in Curve 1. This indicates that the water remaining is bound with greater tenacity than that in the sample with 13 percent moisture whose peak is at 117°C. in Curve 2. Curve 3 shows that the sample with 30 percent moisture loses its water most

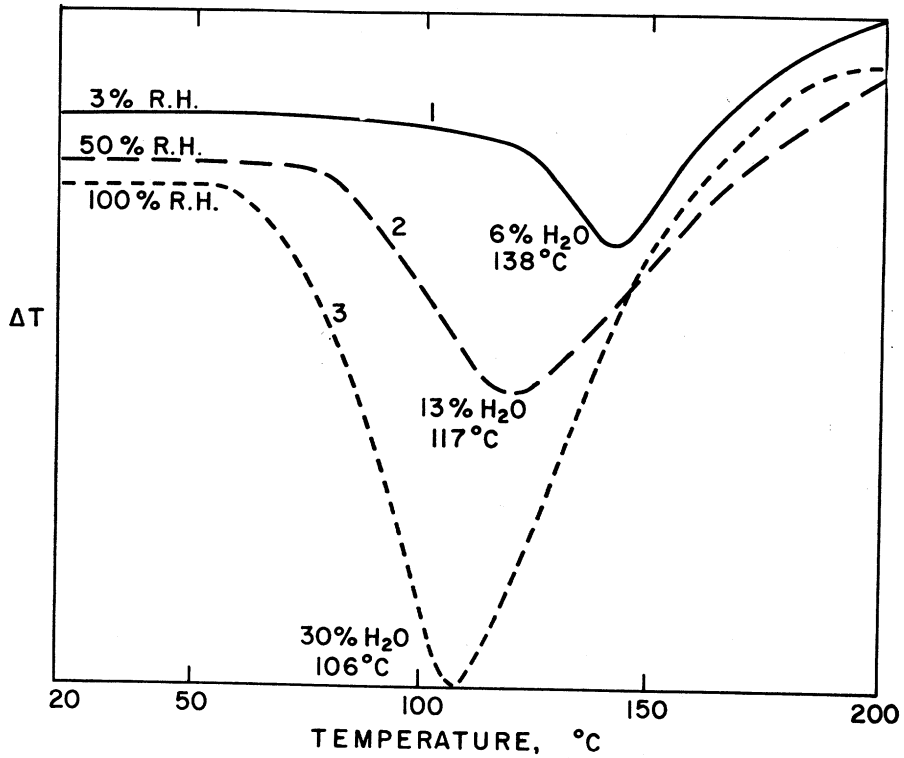

FIGURE 3.—Bound water DTA thermograms of chrome-tanned leather after conditioning treatments.

readily on heating. The peak temperature is 106°C. All the preceding thermograms were obtained at atmospheric pressure. Just as water under pressure or vacuum boils at temperatures other than 100°C., likewise the peak due to bound water in leather would be expected to shift with change in pressure.

Figure 4 illustrates thermograms obtained under vacuum. Curve 1 is a thermogram of a leather sample with peak temperature of 117°C. at 760 mm atmospheric pressure. Under 490 mm vacuum the peak has shifted to 108°C. and under 256 mm vacuum to 96°C. Some measurements under pressures higher than atmospheric pressure were made in the pressure cell previously mentioned. As would be expected, these pressures produced peak temperatures higher than 117°C., just as the use of vacuum produced lower peak temperatures. But as the water is lost

from the leather sample under pressure, some of it recondensed in the closed system, producing two peaks. For this reason, most of the temperature-pressure data was obtained on systems under vacuum.

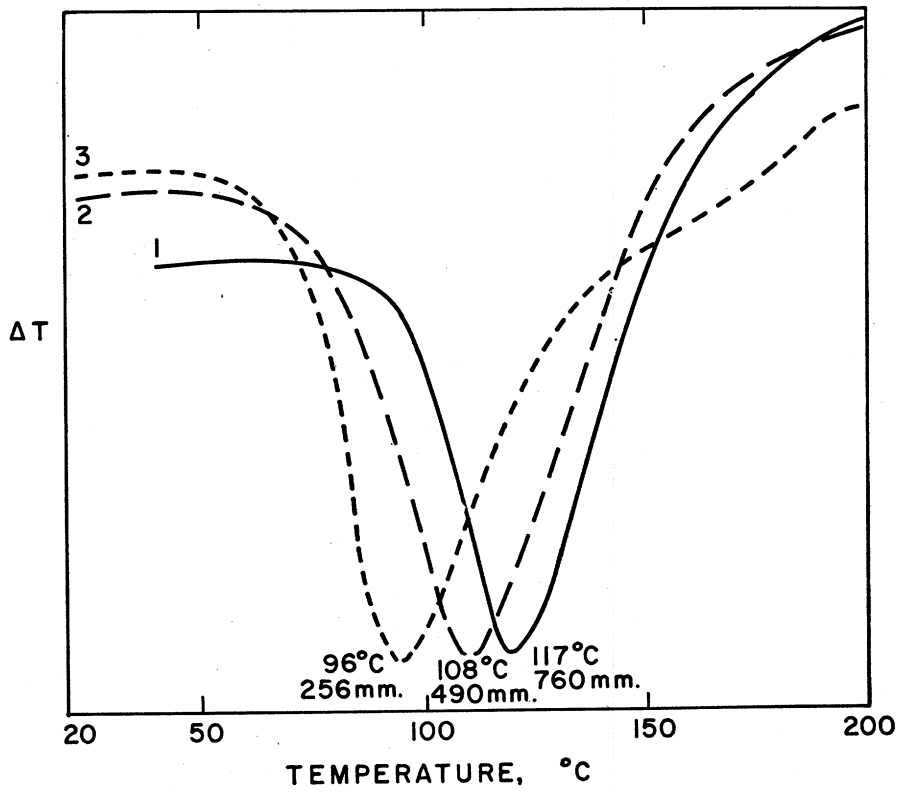

FIGURE 4.—Bound water DTA thermograms of chrome-tanned leathers at atmospheric pressure and under vacuum.

Calculation of the Heat of Dehydration ($\triangle H$).—The relationship between transition temperature T and pressure P is given by the Clausius-Clapeyron equation, the integrated form of which is written

$$\ln P = -\frac{\triangle H}{R}\left(\frac{1}{T}\right) + \text{Constant}$$

where ln P = natural logarithm of pressure in millimeters of mercury, $\triangle H$ = heat of dehydration in Kcal/mole, R = gas constant 1.987×10^{-3} Kcal/°K/mole, T = temperature in °K, and the constant is related to the entropy change of the transition. A plot of the natural log of pressure against the reciprocal of temperature will yield a straight line, the slope of which is $-\frac{\triangle H}{R}$. Thus a

value for $\triangle H$ is a "peak temperature heat of dehydration" for the leather water system. We call the $\triangle H$ a "peak temperature heat of dehydration" because it is calculated from the peak temperature which seems to represent the energy level of the greatest number of water molecules in our binding energy spectrum. It is not truly an average because it is not found at the midpoint of the temperature range covered. It is by no means a maximum because not all of the water has been removed from the sample at the peak temperature because (a) the residual water remaining at low humidities is lost at temperatures above that of the peak and (b) the thermogram does not immediately return to its baseline after passing the peak temperature, indicating that thermal changes are still taking place.

To test the validity of applying the Clausius-Clapeyron equation to the present system we first applied it to the heat of vaporization of water itself. The boiling points of water were determined at three different pressures and a plot of the natural log of pressure versus the reciprocal of temperature was drawn. The result was a straight line, the slope of which determined by a least squares calculation was 9.83 Kcal/mole. The literature value for the heat of vaporization of water between 71 and 121°C. is 9.74 Kcal/mole, an error of less than one percent.

Figure 5 shows a typical pressure-temperature diagram for a fresh corium split of an acetone-dehydrated calfskin, conditioned to reach the various moisture levels listed. Measurements were made using both pressure and vacuum. Samples with the lowest moisture levels have the highest $\triangle H$ values, that is, more energy is required to remove the bound water. The difference in $\triangle H$ values between samples containing 16 and 43 percent water is not as great as that between the samples containing four and 16 percent water. This means that the water remaining required more energy to remove. The least energy is required to break the bonds in samples containing 43 percent water.

Table I shows $\triangle H$ values obtained for a cross-section of commercially tanned leathers stored at 50 percent R.H. and 23°C. Values for acetone dehydrated calfskin, reconstituted collagen, gelatin, and oxalic acid are included for comparison. Since some of the values listed for leathers are based on runs on one example of a particular tannage, we should not cite our values as typical for any particular tannage but they are striking in their similarity. The $\triangle H$ values of all the leather samples illustrated here after conditioning at 50 percent R.H. are of the same order of magnitude. Differences may well be within the error of reading temperatures from such broad peaks. The $\triangle H$ values are about the same for both tanned leathers and untanned hides and do not vary with tanning agents or finishes. Only the value obtained for the sample of reconstituted collagen is slightly lower. Reconstituted collagen presented a storage and conditioning problem because the bound water peak shifts more rapidly with time, even at 50 percent R.H. where leather samples change very slowly. Because of the many variables

involved (time, solubilization procedures, reconstitution procedures, residual ions, etc.), reconstituted collagen represents a research problem in itself and was not investigated further.

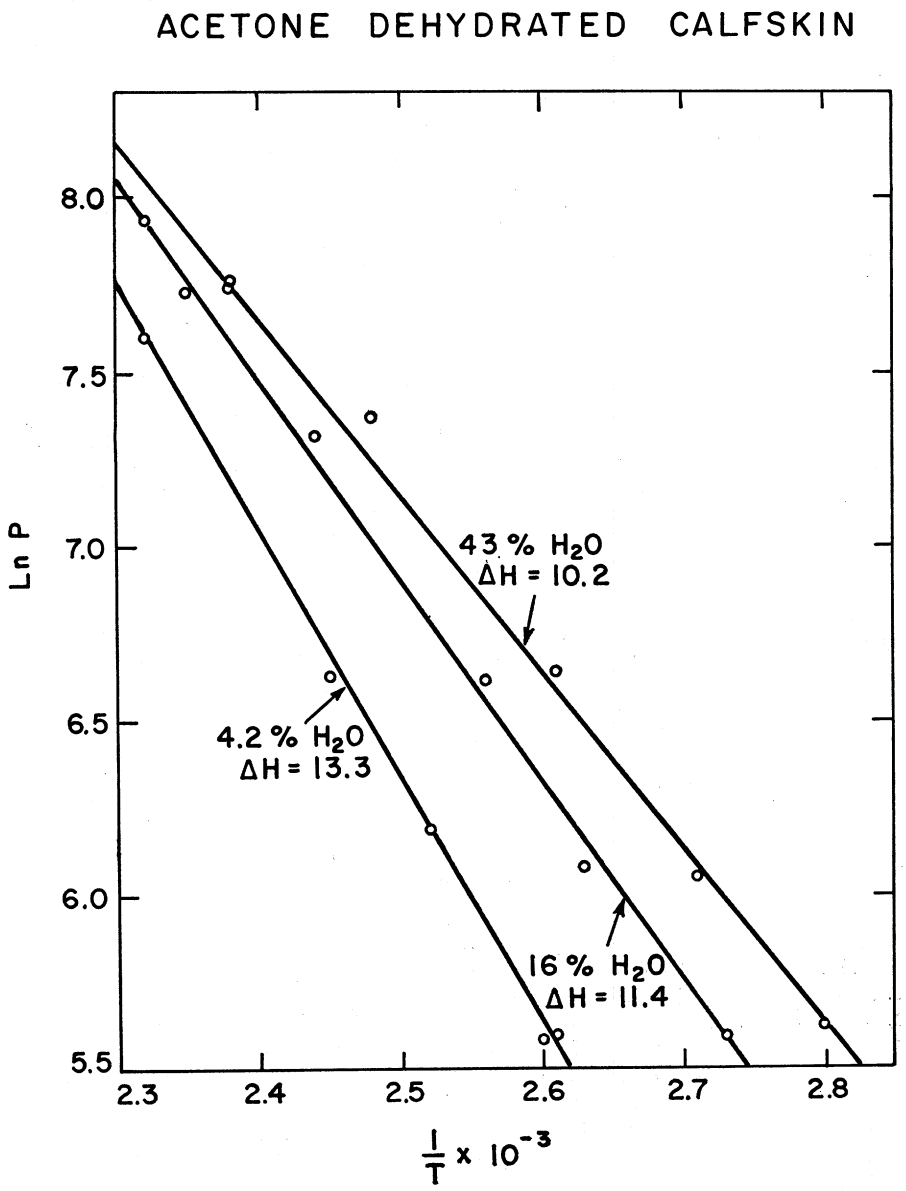

FIGURE 5.—Pressure temperature diagram of acetone dehydrated calfskin.

All of the hide materials listed in Table I have $\triangle H$ values higher than the $\triangle H$ obtained for liquid water, 9.83 Kcal/mole. This means that more energy is required for dehydration of the collagen system than for water itself, indicating stronger binding. Gelatin has a still higher $\triangle H$ value, 18.5 Kcal/mole. The gelatin substrate possesses more available sites for water binding because of previous breakdown from collagen, hence the higher value. The $\triangle H$ for a crystalline hydrate, oxalic acid, is 23 Kcal/mole, more than double that of liquid water. Thus the $\triangle H$ values for collagen-water and gelatin-water systems lie between those for liquid water and water bound in a crystalline hydrate.

TABLE I

$\triangle H$ VALUES FOR HIDE MATERIALS CONDITIONED AT 50% R.H. AND 23°C.

Sample Description	H_2O %	$\triangle H$ Kcal/mole
Chrome-tanned side upper leather	13.3	11.0
Chrome-tanned glutaraldehyde-retanned silicone treated side upper leather	14.6	12.6
Chrome-tanned vegetable-retanned side upper leather	13.7	12.5
Chrome-tanned bleached side upper leather	11.6	12.2
Chrome-tanned vegetable-retanned side upper leather	14.3	11.8
Chrome-tanned vegetable-retanned side upper leather	13.8	12.4
Chrome-tanned mordanted with vegetable extract side upper leather	15.4	12.3
Vegetable-tanned sole leather	11.5	12.1
Acetone dehydrated calfskin	15.6	11.4
Reconstituted collagen	10.8	10.3
Gelatin	9.5	18.5
Oxalic acid	28.6	23.0

REFERENCES

1. Roddy, W. T. *Chemistry and Technology of Leather,* Ed. O'Flaherty, F., Roddy, W. T., and Lollar, R. M., Vol. 4, Chapter 50, Reinhold, New York (1965).
2. Anonymous. *Chemistry,* **39**, 26 (1966).
3. Sussman, M. V., and Chin, L. *Science,* **151**, 324 (1966).
4. Witnauer, L. P., and Wisnewski, A. *JALCA,* **59**, 598 (1964).
5. Naghski, J., Wisnewski, A., Harris, E. H., Jr., and Witnauer L. P. *JALCA,* **61**, 64 (1966).
6. Wisnewski, A. M., Calhoun, R. J., Jr., and Witnauer, L. P. *J. Appl. Pol. Sci.,* **9**, 3935 (1965).

DISCUSSION

MR. RODDY: Thank you very much, Mrs. Jahn.

From the data you presented, it is very noticeable that hide or leather shrinks first, and then melts. The first notable shrinkage in chrome-tanned leather from which water has been removed apparently begins at 75°C. This suggests an entirely different response from that which occurs in excess water, as the shrinkage temperature is normally run. The DTA indicates the beginning temperature, the onset, and then the melting point temperature, and it definitely gives a range before you have melting.

In 1964 when the first observation was made by your group on DTA, in discussion it was mentioned that a study should be made to arrive at a practical shrinkage temperature value. Do you now feel that you can predict whether the onset or the peak temperature is important as the shrinkage temperature value?

MRS. JAHN: The onset temperature is a very difficult measurement to make. It is not reproducible, and it is often difficult to measure accurately. The peak temperature is a maximum point of the reaction, and therefore this should be used as the DTA measurement of shrink temperature.

There is another value which can give you some information, and this is the extrapolated onset temperature. You can extrapolate the longest line segments of the descending curve with a line which goes out from the base line. This will be higher than the onset temperature and lower than the peak temperature; however, the peak temperatures represent the maximum shrinkage reaction although this is not true in the bound water measurement.

There is a difference between the shrinkage temperatures, and the bound water peaks as we have determined here. The difference is that the shrinkage temperatures are determined in excess of water. They cannot be determined reproducibly by DTA methods without an excess of water which we usually use at 50 percent.

The bound water peaks were obtained in leather samples, not dried, but as they exist in the particular humidity at which they have been conditioned.

MR. RODDY: I should like to ask you one more question. If deterioration of hide occurs at the onset temperature or at the peak temperature is only water being removed during this period of increasing temperature? You indicated for example the fibrillar structure is not altered, but on the other hand, we do know you are removing some water, and the leather will definitely shrink and we see this visually.

MRS. JAHN: But the samples are still able to accept some water, and in this particular case, we have not added any water to the samples so we find the normal fiber structure is still present at the end.

MR. RODDY: Are there any questions from the audience on this paper? If not, thank you very much for your good presentation.